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(54) Title: FLUORINE-CONTAINING COPOLYMER

(57) **Abstract:** A fluorine-containing copolymer obtained by copolymerizing tetrafluoroethylene, hexafluoropropylene and perfluoro vinyl ether as component monomers, wherein a weight ratio of tetrafluoroethylene, hexafluoropropylene and perfluoro vinyl ether units constituting the fluorine-containing copolymer is 70 to 95 : 5 to 20 : 0 to 10, respectively; the fluorine-containing copolymer having: a melt flow rate of 30 (g/10 minutes) or more; a volatile content index of 0.2 % by weight or less; and a stress relaxation modulus G(t) (unit: dyn/cm) which satisfies the following formula at t = 0.1 second when measured at a temperature of 310 : G(0.1) > 7 ~ 10 ~ X - 3000 where X denotes the melt flow rate (unit: g/10 minutes). Also disclosed is an insulating material composed of the fluorine-containing copolymer and an insulated cable having a core conductor coated with the fluorine-containing copolymer.

WO 03/059970 A1

DESCRIPTION

FLUORINE-CONTAINING COPOLYMER

CROSS REFERENCE TO RELATED APPLICATIONS

5   This application is a continuation-in-part of U.S.
Application No. 10/046,703 filed on January, 17, 2002, the
disclosure of which is incorporated herein by reference.

TECHNICAL FIELD

10   The present invention relates to a fluorine-containing
copolymer which improves extrusion moldability for coating an
electric cable with an insulating resin and which is capable
of suppressing the occurrence of molding faults over long term
operation even when coating at high speed.

15

BACKGROUND ART

Tetrafluoroethylene (TFE)/hexafluoropropylene (HFP)
copolymer has superior heat resistance, chemical resistance,
extrusion moldability and the like, and in addition, has

20   superior electric insulating property and high-frequency
property with a low dielectric tangent. Therefore, it is used
for insulating cable such as a cable and a wire, and such
insulated cable is suitably used as a communication cable. The
communication cable includes a data transmission cable such as

25   a LAN cable.

TFE/HFP copolymer also has low flammability and low
smoking properties. Thus, insulated cable made from such a
copolymer can be used as a plenum cable, which is laid, for
example, on the back of a ceiling of a building (plenum area)

30   and strictly regulated for preventing the spread of fire.
The insulated cable comprises a core wire such as a cable and
an insulating material formed from a resin such as a TFE/HFP
copolymer coating the core wire. In general, the insulated
cable is manufactured by extrusion coating in which molten resin

35   is extruded in the shape of a tube, drawn down by inserting a

core wire through the center portion of the resin tube in its axial direction, and the core wire coated with the resin is then taken up.

The term "draw-down" as used herein means extending a
5   molten resin extruded from a die having an opening of relatively large sectional area to its final intended dimensions. The draw-down is characterized by a draw-down ratio (DDR), which is the ratio of the sectional area of the opening of the die to the sectional area of the insulated material of the final
10   product. In general, the draw-down ratio is suitably from 50 to 150.

The term "insulated" cable as used herein means a cable or wire coated with an insulating material.

Preferably, the draw-down operation is carried out in so
15   that the outer side and inner side of the molten resin, extruded from the die in the form of a tube, are evenly drawn down. This evenness is expressed as draw ratio balance (DRB).

Since in a conventional draw-down operation the resin is drawn as described above, a cone-break sometimes occurs during
20   an extremely short period between the time the resin is extruded from an opening of the die until it contacts a core material. The cone-break is the largest cause of loss in productivity. This is because cone breaks, when they occur, requires restarting the extrusion process and machine utilization is
25   decreased.

In recent years, an increase in molding rate has been desired to enhance productivity and to reduce cost, and there is a demand to increase the cable coating rate by increasing the winding rate of the insulated core wires. The trend of
30   coating the cable at high speed generally increases the occurrence of cone-breaks even though the draw-down ratio is similar.

A technique for reducing the occurrence of cone-breaks is proposed in Publication No. WO 00/44797, in which a TFE/HFP
35   copolymer having a melt flow rate (MFR) of 24 (g/10 minutes)

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is used and the coating rate of applying an insulating resin
to the cable is lower than 2000 ft/minute. Indeed, this
copolymer is effective at a coating rate of lower than 2000
ft/minute. However, this technique does not satisfactorily
5   reduce the occurrence of cone-breaks at faster coating rates.

In the coating extrusion, the thickness of the insulating
material of the insulated cable is determined by the desired
electrical characteristic, and the size of the opening of the
die is determined by selecting a draw-down ratio and draw ratio
10   balance suitable for the structure of the insulated cable.

In the case of increasing the cable coating rate without
changing the size of the opening of the die, the problem of
developing a rough skin on the surface of the resin passing
through the opening generally occurs when the velocity of the
15   molten resin in the die exceeds a certain velocity limit. This
rough skin is referred to as melt fracture, and it develops when
the velocity of the resin exceeds the critical shear rate during
melt fluidizing.

The trend of coating cable at high speed also involves
20   the problem of exacerbating the extent of the melt fracture.
Excessive melt fracture sometimes leads to a situation where
the insulating material does not completely cover the core
material, and causes an increase in molding faults such as
spark-out and cone-breaks.

25   As one technique for delaying the occurrence of melt
fracture and enabling high-speed coating of about 1.5 times
faster than conventional rates, U.S. Patent No. 5,703,185
discloses that vinyl ether for use as a third monomer component
of a TFE/HFP copolymer is changed from perfluoro (propyl vinyl
30   ether) to perfluoro (ethyl vinyl ether). However, this
technique encounters difficulty in reducing molding faults such
as cone-breaks and the like at high-speed coating rates.

SUMMARY OF THE INVENTION
35   It is therefore an object of the present invention to

provide a fluorine-containing copolymer which improves extrusion moldability for coating an electric cable with an insulating resin, and which is capable of considerably reducing molding faults such as spark-out and cone-breaks over long term operation even when coating at high speed.

The above object of the present invention is achieved by providing a fluorine-containing copolymer obtained by copolymerizing tetrafluoroethylene, hexafluoropropylene and optionally perfluoro vinyl ether as component monomers, wherein a weight ratio of tetrafluoroethylene, hexafluoropropylene and perfluoro vinyl ether units constituting said fluorine-containing copolymer is 70 to 95 : 5 to 20 : 0 to 10, respectively;

the fluorine-containing copolymer having:

a melt flow rate 30 (g/10 minutes) or more:

a volatile content index of 0.2 weight % or less; and

a stress relaxation modulus $G(t)$ (unit: dyn/cm^2) which satisfies the following formula at $t = 0.1$ second when measured at a temperature of 310 °C:

$$G(0.1) > 7 \times 10^6 \times X^{-1.62} - 3000$$

where X denotes the melt flow rate in units of g/10 minutes.

The present invention is a fluorine-containing copolymer obtained by copolymerizing tetrafluoroethylene, hexafluoropropylene and optionally perfluoro vinyl ether as component monomers, wherein a weight ratio of tetrafluoroethylene, hexafluoropropylene and perfluoro vinyl ether units constituting said fluorine-containing copolymer is 70 to 95 : 5 to 20 : 0 to 10, respectively;

the fluorine-containing copolymer having:

a melt flow rate 30 (g/10 minutes) or more:

a volatile content index of 0.2 weight % or less; and

a stress relaxation modulus $G(t)$ (unit: dyn/cm^2) which satisfies the following formula at $t = 0.1$ second when measured at a temperature of 310 °C:

$$G(0.1) > 7 \times 10^6 \times X^{-1.6143} - 3000$$

where X denotes the melt flow rate in units of g/10 minutes.

Hereinafter, the present invention will be described in greater detail.

DETAILED DESCRIPTION OF THE INVENTION

The fluorine-containing copolymer of the present invention is suitably used for coating a core wire with an insulating resin by extrusion processing. The above-mentioned fluorine-containing copolymer is melted by heating within an extruder for coating a core wire and extruded from a die, and then drawn down by coating the core wire to thereby obtain an insulated wire.

In the present specification, the speed at which the core wire coated with insulation by the above extrusion processing is reeled up is referred to as the "coating speed". The coating speed is expressed by the length of insulated core wire reeled up over a period of one minute (expressed by feet "ft").

The fluorine-containing copolymer of the present invention advantageously reduces the occurrence of molding faults such as cone-breaks and spark-out, particularly in the case where the coating operation is carried out at a high-speed of, e.g., 2500 ft/minute or higher.

The fluorine-containing copolymer of the present invention is obtained by copolymerizing tetrafluoroethylene (TFE), hexafluoropropylene (HFP) and perfluoro vinyl ether (PVE) as component monomers.

The above-mentioned perfluoro vinyl ether is an optional component, and in a preferred embodiment the fluorine-containing copolymer of the present invention may be a binary copolymer made up of only TFE and HFP units. As used herein, the above-mentioned binary copolymer excluding PVE is referred to as "non-modified FEP".

The fluorine-containing copolymer of the present invention may be a ternary copolymer containing a small number

of perfluoro vinyl ether units (e.g., from 0.1 to 10 wt%) in addition to TFE and HFP units. As used herein, the ternary copolymer is referred to as "modified FEP". One, two or more species of the above-mentioned perfluoro vinyl ether may be

5   used.

The above-mentioned perfluoro vinyl ether is not particularly limited and, for example, includes an unsaturated perfluoro compound represented by the following general formula:

10 $CF_2 = CF - ORf^1$
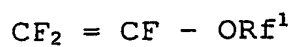
where Rf^1 is a perfluoroaliphatic hydrocarbon group. As used herein, a perfluoroaliphatic hydrocarbon group means an aliphatic hydrocarbon group in which all hydrogen atoms linked to the carbon atoms are replaced with fluorine atoms. The

15 above-mentioned perfluoroaliphatic hydrocarbon group may have one or more ether oxygens.

An example of the above-mentioned perfluoro vinyl ether includes perfluoro(alkyl vinyl ether) (PFAVE). PFAVE is a compound represented by the following general formula:
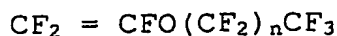
20 $CF_2 = CFO(CF_2)_nCF_3$

where n is an integer of 0 to 3. One, two or more species of PFAVE may be used. As PFAVE, perfluoro(ethyl vinyl ether) (PEVE) and perfluoro(propyl vinyl ether) (PPVE) are preferred, and PPVE is more preferred since it can readily increase the

25 speed of the coating extrusion.

Preferred fluorine-containing copolymers of the present invention include modified FEP in which PFAVE is used as the above-mentioned perfluoro vinyl ether in terms of enhancing resistance to stress cracks and enabling high-speed extrusion

30 for coating cable and wire.

A weight ratio of TFE and HFP, and as needed PFAVE, as component monomers of the fluorine-containing copolymer of the present invention is not particularly limited so long as the fluorine-containing copolymer having the properties described

35 below are attained. The weight ratio of TFE, HFP and PFAVE is

70 to 95 : 5 to 20 : 0 to 10, respectively. When the weight
ratio lies within the above-mentioned range, draw-down can be
performed sufficiently while maintaining resistance to stress
cracks. More preferably, the weight ratio is 75 to 95 : 5 to
5   20 : 0 to 5, respectively. The above-mentioned content of TFE,
HFP and PFAVE as component monomers is also referred to as a
monomer composition.

The fluorine-containing copolymer of the present
invention has an MFR of 30 (g/10 minutes) or larger. The
10   above-mentioned fluorine-containing copolymer can lower the
pressure of a molten polymer passing through the die and reduce
the shearing stress of the polymer. This is because the
molecular weight is not high when the MFR lies within the
above-mentioned range. Therefore, it is possible to delay the
15   occurrence of the melt fracture, and it becomes possible to
increase the coating rate. Further, when the MFR lies within
the above-mentioned range, since the polymer is easily
self-fluidized until cooled after being extruded from the die,
the surface of the resulting insulating material becomes smooth.
20   Therefore, it is possible to attain an insulated cable or wire
which does not show traces of melt fracture and which exhibits
less variation in outer diameter. Thus, a product exhibiting
less fluctuation in capacitance is obtained. When the MFR is
less than 30 (g/10 minutes), since the extent of melt fracture
25   becomes intense and cone-breaks and spark-out resulting
therefrom easily develop, it is difficult to coat the cable at
high speed. The MFR is preferably (30 to 50) (g/10 minutes)
in terms of easily allowing for the above-mentioned first
coating rate, and more preferably (30 to 45) (g/10 minutes).
30   The MFR is an index of melt-fluidity. Even though
conventional coating extrusion is performed at a lower speed
than the faster rate in accordance with the present invention,
melt fractures often develop. It is generally considered that
the shearing stress when passing the molten polymer through the
35   die will increase and the extent of the melt fracture will become

high when the coating rate is increased. However, in accordance
with the present invention, by having an MFR within the
above-mentioned range, it is possible to restrain the
occurrence of melt fracture as described above even when coating

5   the cable at high speed.

The fluorine-containing copolymer of the present
invention has a stress relaxation modulus $G(t)$ (unit: dyn/cm^2)
which satisfies the following formula at $t = 0.1$ second when
measured at a temperature of 310 °C:

10   $G(0.1) > 7 \times 10^6 \times X^{-1.62} - 3000$,

where X denotes the melt flow rate (unit: g/10 minutes). The
above fluorine-containing copolymer can maintain molding
stability without developing molding faults such as cone-breaks
and spark-out over long term operation even in the case of

15   coating the cable at high speed when the stress relaxation
modulus thereof is within the ranges described above.
Preferably, the stress relaxation modulus satisfies the
following formula at $t = 0.1$ second when measured at a
temperature of 310 °C:

20   $G(0.1) > 7 \times 10^6 \times X^{-1.6143} - 3000$,

more preferably, the stress relaxation modulus satisfies the
following formula at $t = 0.1$ second when measured at a
temperature of 310 °C:

$G(0.1) > 7 \times 10^6 \times X^{-1.62}$, and

25   still more preferably, the stress relaxation modulus satisfies
the following formula at $t = 0.1$ second when measured at a
temperature of 310 °C:

$G(0.1) > 7 \times 10^6 \times X^{-1.6143}$.

The stress relaxation modulus is a value obtained by

30   measuring at a certain point in the process where the stress
developed inside decreases with time after applying strain.
When the fluorine-containing copolymer satisfies the
above-mentioned formula, it can control the occurrence of
molding faults. This is because the polymer can withstand the

35   stretching stress applied until the polymer coats the conductor

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by extruding the polymer from the die even in the case of coating the cable at high speed. Preferably, the upper limit of the stress relaxation modulus at t = 0.1 second when measured at a temperature of 310 °C (G(0.1)) is 100000, since the stretching
5   stress of the fluorine-containing copolymer is not too high and draw-down can be performed sufficiently so that the occurrence of molding faults can be reduced when the fluorine-containing copolymer has the MFR of 30 (g/10 minutes) or larger.

The fluorine-containing copolymer of the present
10   invention has a volatile content index of 0.2 % by weight or less. When the volatile content index lies within the above-mentioned range, minute bubbles do not develop in the above-mentioned insulating material, and therefore the fluorine-containing copolymer does not cause molding faults
15   such as spark-out and cone-breaks even in the case of coating the cable at high speed. When the volatile content index exceeds 0.2 % by weight, minute bubbles develop in the above-mentioned insulating material and cause melt fractures such as spark-outs and cone-breaks accompanying the thin
20   insulation due to draw-down. Therefore, moldability becomes unstable and it becomes difficult to coat the cable at high speed.

The volatile content generally results from any of a functional group at the end of the polymer, which is unstable
25   at an elevated temperature, a substance formed by decomposition of a polymer main chain, an oligomer produced in polymerization and residuals due to a lack of deaeration in melt-pelletizing.

Preferably, the fluorine-containing copolymer of the present invention has a melting point of 245 to 280 °C. Such
30   a fluorine-containing copolymer has sufficient melt-fluidity at normal molding temperatures, and is capable of having a wide molding region while maintaining heat resistance. More preferably, the melting point thereof is 245 to 260 °C.

The process for producing the fluorine-containing
35   copolymer of the present invention is not particularly limited,

and may be produced by polymerizing the monomer components using
conventional polymerization processes such as emulsion
polymerization, suspension polymerization, solution
polymerization, bulk polymerization and gas-phase
polymerization.

     Examples of a chain transfer agent that can be used to
polymerize the monomer components include a liquid chain
transfer agent such as isoparaffin, carbon tetrachloride,
diethyl malonate, mercaptan, diethyl ether, alcohol and the
like. Further, a gaseous chain transfer agent such as methane,
ethane and the like can be used.

     Ammonium persulfate and/or potassium persulfate can be
used as a polymerization initiating agent to start the
polymerization reaction by initial charging. Although the
initially charged polymerization initiating agent is consumed
or decomposed with progression of the reaction from just after
the start of the reaction, by continuously adding an appropriate
amount, the molecular weight, molecular weight distribution and
the like can be controlled.

     If suspension polymerization is used, diacyl peroxide is
preferably used as the polymerization initiating agent. A
suitable polymerization initiating agent is a fluorine-
containing peroxide expressed by the formula:

$$(Rf^2COO)_2$$
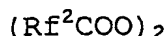
where Rf^2 is a perfluoroalkyl group, a hydrofluoroalkyl group
or a perchlorofluoroalkyl group.

     The fluorine-containing compound of the present
invention is used in any form of powder, pellet and the like
in the extrusion processing, but is generally used in pellet
form.

     A method of preparing the above-mentioned pellet is not
particularly limited, and a conventionally known method, for
example, may be used. One method, for example, of pelletizing
the resin powder obtained by the above-mentioned polymerizing
method comprises using an extruder and heating the resin powder,

for example, to a temperature higher than the melting point of the above-mentioned fluorine-containing copolymer and lower than the decomposition temperature of the fluorine-containing copolymer to melt and knead the resin.

5   The above-mentioned pellet may be formulated with other components together with the fluorine-containing copolymer as needed. Such additional components are not limited in particular, and additives such as various fillers, stabilizers, lubricants, crosslinking agents and other conventional
10   additives may be used.

In the method of producing the above-described pellets, the fluorine-containing copolymer of the present invention may be adjusted to attain a stress relaxation modulus, volatile content index, MFR and melting point within the above-mentioned
15   ranges by using the method, for example, as described below.

The above-mentioned fluorine-containing copolymer can be adjusted to have a stress relaxation modulus satisfying the above formula by adjusting molecular weight, distribution of molecular weight, extent of entanglement of high polymers,
20   branching of high polymers, the degree of cross linkage, polymer composition and the formulation of additives.

The fluorine-containing copolymer can be adjusted to have a volatile content index within the above-mentioned range by carrying out end stabilization of unstable ends as required.
25   The end stabilization includes, for example, heat-treating in fluorine gas, adding a chain transfer agent during polymerization and heat-treating after emulsion polymerization. It is also possible to adjust the extent of end stabilization by adjusting the addition amount of the chain
30   transfer agent and the addition time thereof, and the temperature and the time period of heat treatment.

The fluorine-containing copolymer can be adjusted to have an MFR and melting point within the above-mentioned ranges by adjusting the molecular weight and the distribution of
35   molecular weight of the fluorine-containing copolymer, by

adjusting the addition amounts of the chain transfer agent and
an initiator during polymerization, or by adjusting the monomer
composition.

    For the fluorine-containing copolymer of the present
invention, when the resin powder obtained by polymerization is
pelletized, it is possible to adjust the extent of reduction
in the volatile content index and increase in MFR by adjusting
the heating temperature, heating time and the like.

    The method of insulating cable or wire of the invention
comprises extrusion coating cable or wire with the above
fluorine-containing copolymer.

    The method of extrusion coating with the
fluorine-containing copolymer of the present invention is not
particularly limited, and, for example, a conventionally
well-known method can be used. A conventional extruder for
coating cables may be used.

    The rate of coating the cable is not limited in particular,
and it is possible to obtain the effect of the invention, which
suppresses molding faults, at coating rates of from 2500 to 3500
ft/minute, and particularly of from 2800 to 3000 ft/minute.

    Needless to say, the fluorine-containing copolymer of the
present invention can also be effectively used at lower coating
speeds, such as less than 2,500 ft/min. which have been employed
in conventional extrusion coating, for example, approximately
1,000 to 2,500 ft/min.

    The insulated cable of the present invention comprises
a core conductor coated with an insulating material comprising
the above fluorine-containing copolymer. The core conductor
can be a no-covering conductor or a conductor with a covering
material e.g. a wire or a cable, to be used as a core of the
insulated cable, and may be referred to as "conductor"
comprising copper etc., "core wire" or "core cable" in this
specification.

    The insulated cable obtained by the above-described
coating extrusion is not particularly limited as long it

includes a core wire and an insulating material coating the same, and includes, for example, a cable, a wire and the like. Among these, the insulated cable is suitably used as an insulated communication wire, for example, a cable connecting a computer
5   and peripherals thereof, including a data transfer cable such as a LAN. It is also suitably used as a plenum cable.

        As used herein, the monomer composition, MFR, stress relaxation modulus, volatile content index and melting point described above are defined or measured as follows.
10 (A)   Monomer Composition

        The monomer composition is obtained by NMR analysis and measuring the contents of TFE, HFP and PFAVE. Further, generally, the monomer composition can also be determined by infrared absorption spectrum analysis as described in Japanese
15 Kokoku Publication Sho-63-2281.

    (B)   MFR

        Using a melt index tester in compliance with ASTM D 1238-98 or JIS K 7210, approximately 6 g of resin is charged in a cylinder having an inner diameter of 0.376 inch and maintained at 372 °C
20 ± 0.5 °C for five minutes until an equilibrium temperature is reached. Then, the molten resin is extruded through an orifice having a diameter of 0.0825 inch and a length of 0.315 inch under a piston load of 5,000 g, and the weight of the resin (unit: g) collected in a unit period of time (usually 10 to 60 seconds)
25 is measured. Three measured values are averaged and converted to the amount of extrusion per 10 minutes as the MFR (unit: g/10 min.).

    (C)   Stress Relaxation Modulus

        The measurement sample is prepared by compression molding.
30 That is, the resin is charged into a die of 25 mm in diameter, and after heating at a temperature of 340 °C for 30 minutes, the molten resin is cooled under an applied pressure of 40 Kg/cm^2, and a sheet having a thickness of 1.5 ± 0.1 mm is prepared.

        A dynamic analyzer RAD II made by Rheometric Scientific
35 Company is used as the measuring apparatus, and Rhios V4.3.2

by the same company is used as analysis software. When
measuring, a pair of parallel plates is selected as a tool, and
a plate having an outer diameter of 25 mm is used.

The measurement is carried out under the following
5   conditions:
distance between the parallel plates: 1.0 mm
test procedure: Dynamic Frequency Sweep Default Test
strain: 0.1 (unit: %)
measuring temperature: 310 °C
10 measuring frequency: 0.1 to 500 rad/sec.

After the sample is placed on the parallel plate and heated
to a measuring temperature of 310 °C, the distance between the
parallel plates is moved so as to be 1 mm. The resin protruding
from the parallel plates is removed, and the measurement is
15 started 100 seconds after the sample again reaches 310 °C.
After completing the measurement, viscosity, storage elastic
modulus and loss of elastic modulus at each frequency are
obtained, and the stress relaxation modulus at 0.1 second is
determined using the Rhios V4.3.2 (Rheometric Scientific
20 Company) as the analysis software.
(D)   Volatile Content Index

Using an electric oven having a turntable, the volatile
content (% by weight) is measured as follows. That is, as a
sample, 20 ± 0.1 g of the above FEP in pellet form is weighed
25 out using a precision balance having an accuracy of 0.1 mg and
in an aluminum cup that has been baked at 370 °C beforehand in
an empty state. The letter A used herein indicates the weight
of the baked aluminum cup and the letter B indicates the weight
of the aluminum cup in which the sample is placed. As for B,
30 two aluminum cups containing a sample per each sample to be
measured are prepared and an average value of the two cups is
used. A standard sample having a known volatilized amount is
also weighed out at the same time as a control. These are
quickly put onto the turntable of the electric oven, which has
35 been heated to 370 °C. At this time, the rotation speed of the

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turntable is 6 rpm.

    30 minutes after the internal temperature is returned to
370 °C, the samples are removed from the oven and quickly put
in a desiccator, in which they are cooled for over an hour. Then,
5   the weight of the sample is precisely weighed using the above
precision scale. The letter C denotes the weight at this time.
The weight reduction of the sample after heating for 30 minutes
at 370 °C is calculated by the following formula and is referred
to as the volatile content index (% by weight):
10 Volatile content index (% by weight) = ((B-C)/(B-A)) × 100
(E)   Melting point
    Using DSC (differential scanning calorimetry) as
described in ASTM D 4591-87, the melting point is measured at
a temperature-rise rate of 10 °C/minute. A peak temperature
15 of an endothermic reaction indicating a maximum is taken as the
melting point.

            BEST MODE FOR CARRYING OUT THE INVENTION
    The present invention is described in further detail by
20 means of the following Examples. However, the present
invention should not be construed as being limited thereto.
Example 1
(Manufacturing of modified FEP powder)
    310 kg of pure water and 200 g of w-hydrofluorocarboxylic
25 acid were charged into a 1,000-L glass lined autoclave having
a stirrer. After purging with nitrogen, a vacuum was
established, and 320 kg of hexafluoropropylene (HFP) and 3 kg
of perfluoro(propyl vinyl ether) (PPVE) as a perfluoro(alkyl
vinyl ether) (PFAVE) were charged thereto. Stirring was
30 started, the temperature of the polymerizing vessel was set at
34.0 °C, and the pressure was increased to 10.5 MPaG with
perfluoroethylene (TFE). Then, when 3.8 kg of
di-(w-hydrodecafluoroheptanol)peroxide (DHP) diluted to
approximately 8 wt% with perfluorohexane was added, the
35 reaction began immediately. During the reaction, TFE was

additionally charged in an amount of 310 kg to maintain the
pressure in the autoclave at 10.5 MPaG. During the reaction,
when the amount of TFE supplied reached 25 wt%, 50 wt% and 75
wt% of the reaction mixture, PPVE was charged in amount of 800

5   g at each time interval. Also, 2 and 4 hours after the start
of the reaction, DHP was added each time in an amount of 3.8
kg, and six hours after the start of the reaction and every two
hours thereafter, DHP was added in an amount of 1.9 kg,
respectively. In order to adjust the molecular weight, 7 hours

10   after the start of the reaction, 4.1 kg of methanol was added
as a chain transfer agent.

　　　After a total reaction time of 24 hours, non-reacted TFE
and HFP were released to obtain a granular powder. Pure water
was added to this powder, and after stirring and washing, it

15   was removed from of the autoclave. The powder was then dried
for 24 hours at 150 °C to obtain 357 kg of the above-mentioned
modified FEP powder.

　　　The resulting modified FEP powder measured as described
above had a composition weight ratio of TFE, HFP and PPVE of

20   87.2 : 11.8 : 1.0.

　　(Pelletization and evaluation of physical properties)

　　　Using a 50 mm-diameter extruder having a barrel to die
temperature set at 360 °C, the above modified FEP powder was
pelletized at a speed of 12 kg/hour, and then deaerated for 8

25   hours at 230 °C.

　　　The respective measurements by the methods described
above on the resulting pellets showed that MFR was 38 (g/10
minutes), the volatile content index was 0.133 % by weight, the
melting point was 256.3 °C and the stress relaxation modulus

30   satisfied the above-mentioned formula. The results are given
in Table 1.

　　(Extrusion coating)

　　　Measurement of spark-out and cone-breaks were measured
by the following method.

35   1)   Conditions of extrusion coating for measurement

The above-mentioned insulated material obtained by
extrusion coating under the following conditions was evaluated.
- standard core wires: AWG 24
- diameter of core wires: 20.1 mil (about 0.51 mm)
5   - thickness of insulation: 7.5 mil (about 0.19 mm)
- diameter of insulated cable: 35.1 mil (about 0.89 mm)
- coating extrusion conditions
cylinder diameter: 50 mm
L/D: 30
10 temperature (°C):
Z1: 338 Z2: 360 Z3: 371 Z4: 382 Z5: 399
CL: 404 AD: 404 HD: 404 DIE: 404
- preheating-temperature of core wires: 165 °C
- cone length: 4.7 cm
15· - length of air cooling: 20 ft
- inner diameter of die: 8.71 mm, outer diameter of tip: 4.75
mm
2)   Measuring methods   '
The spark-out of the above-mentioned insulated material
20 was measured using a Model HF-20-H (measuring voltage 2.0 KV)
instrument made by CLINTON INSTRUMENT COMPANY.
The occurrence of cone-breaks of the above-mentioned
insulated material was measured using a KW 32 TRIO instrument
made by Zumbach Co. The instrument was set to detect a diameter,
25 being 50 mil (about 1.2 mm) or more, larger than the nominal
outer diameter of the insulated wire, and the number of the
cone-breaks was measured.
The coating extrusion was performed at respective rates
of 1600, 2000, 2400, 2800 and 3000 ft/minute under the
30 above-mentioned conditions, and the number of spark-outs and
cone-breaks per 1,000,000 ft of the insulated wire thus prepared
was measured. The results are given in Table 2.

Example 2
35   The same method as described in Example 1 was used, except

17

for changing the temperature of the polymerization bath to 35 °C,
the addition amount of methanol to 1.3 kg, the methanol-addition
time to 12 hours following initiation of the reaction, and the
total reaction time to 30 hours. Also, PPVE was not added.

5

Example 3
        The same method as described in Example 1 was used, except
for changing the temperature of the polymerization bath to 35 °C,
the addition amount of methanol to 2 kg, the methanol-addition
10   time to 13 hours following initiation of the reaction, and the
total reaction time to 28 hours.

Example 4
        The same method as described in Example 1 was used, except
15   for changing the methanol-addition time to 10 hours following
initiation of the reaction.

Example 5
        The same method as described in Example 1 was used, except
20   for changing the addition amount of methanol to 4.4 kg, and the
methanol-addition time to 10 hours following initiation of the
reaction.

Example 6
25   The same method as described in Example 1 was used, except
for changing the addition amount of methanol to 4.2 kg, and the
methanol-addition time to 10 hours following initiation of the
reaction.

30   Comparative Example 1
        The same method as described in Example 1 was used, except
for changing the addition amount of methanol to 3.4 kg and the
total reaction time to 22 hours.

35   Comparative Example 2

The same method as described in Example 2 was used, except for changing the addition amount of methanol to 1 kg.

Comparative Example 3
The same method as described in Example 1 was used, except for changing the addition amount of methanol to 3.4 kg, the methanol-addition time to 5 hours following initiation of the reaction, and the extrusion rate in pelletizing to 50 kg/hr.

Comparative Example 4
The same method as described in Example 1 was used, except for changing the addition amount of methanol to 3.4 kg and the methanol-addition time to 5 hours following initiation of the reaction.

Comparative Example 5
The same method as described in Example 1 was used, except for changing the addition amount of methanol to 4.4 kg, the methanol-addition time to 5 hours following initiation of the reaction, and the total reaction time to 22 hours.

Comparative Example 6
The same method as described in Example 1 was used, except for changing the addition amount of methanol to 2.0 kg, the methanol-addition time to 7 hours following initiation of the reaction, and the total reaction time to 22 hours.

Comparative Example 7
The same method as described in Example 1 was used, except for changing the addition amount of methanol to 3.4 kg, the methanol-addition time to 10 hours following initiation of the reaction, and the total reaction time to 22 hours.

Comparative Example 8
The same method as described in Example 1 was used, except

for changing the addition amount of methanol to 3.4 kg, and the methanol-addition time to 7 hours following initiation of the reaction.

Table 1

		Example						Comparative Example							
		1	2	3	4	5	6	1	2	3	4	5	6	7	8
Polymerization															
Water	(kg)	310	310	310	310	310	310	310	310	310	310	310	310	310	310
Reaction temperature	(°C)	34	35	35	34	34	34	34	35	34	34	34	34	34	34
HFP	(kg)	320	320	320	320	320	320	320	320	320	320	320	320	320	320
Pressure	(MpaG)	10.5	10.5	10.5	10.5	10.5	10.5	10.5	10.5	10.5	10.5	10.5	10.5	10.5	10.5
PPVE (initial)	(kg)	3	0	3	3	3	3	3	0	3	3	3	3	3	3
PPVE (every charge)	(g)	800	0	800	800	800	800	800	0	800	800	800	800	800	800
DHP (initial, 2 hrs & 4 hrs after start of reaction)	(kg)	3.8	3.8	3.8	3.8	3.8	3.8	3.8	3.8	3.8	3.8	3.8	3.8	3.8	3.8
DHP (6 hrs after start of reaction and subsequently)	(kg)	1.9	1.9	1.9	1.9	1.9	1.9	1.9	1.9	1.9	1.9	1.9	1.9	1.9	1.9
Methanol	(kg)	4.1	1.3	2	4.1	4.4	4.2	3.4	1	3.4	3.4	4.4	2	3.4	3.4
Methanol-addition time after reaction	(hour)	7	12	13	10	10	10	7	12	5	5	5	7	10	7
Total reaction time	(hour)	24	30	28	24	24	24	22	30	24	24	22	22	22	24
Yield	(kg)	357	350	362	357	357	355	358	350	357	357	353	356	358	358
Pelletizing															
Extrusion temperature	(°C)	360	360	360	360	360	360	360	360	360	360	360	360	360	360
Extrusion rate	(kg/hour)	12	12	12	12	12	12	12	12	50	12	12	12	12	12
Deaeration time	(hours)	8	8	8	8	8	8	8	8	8	8	8	8	8	8
Pellet characteristics															
MFR	(g/10 min.)	38.0	32.0	44.0	31.0	42.0	35.0	24.0	27.0	35.6	36.0	42.0	20.0	20.0	25.0
HFP/PPVE	(wt %)	11.8/1.0	13.7/0.0	13.0/0.9	11.9/0.9	11.8/0.9	11.8/1.0	11.7/1.0	13.7/0.0	11.8/1.0	11.7/0.9	11.8/0.9	11.8/1.0	11.7/0.9	11.6/1.0
Melting point	(°C)	256.3	250.1	248.3	254.3	258.2	257.8	255.3	250.5	257.1	256.8	257.9	256.5	257.0	256.3
Volatile content index	(wt %)	0.133	0.123	0.148	0.105	0.120	0.111	0.128	0.138	0.238	0.146	0.103	0.095	0.105	0.120
*1) $G(t)_1 = 0.1$	(dyn/cm²)	21118	28005	15602	48768	31528	38568	44867	36578	25666	16988	10877	38728	67638	19231
*2) $7 \times 10^6 \times X^{1.62}$	(dyn/cm²)	19313	25513	15230	26859	16422	22065	40659	33596	21466	21081	16422	54630	54630	38057

*1) indicates measured values and *2) indicates calculated value.

Table 2

Number of spark-outs and cone-breaks per 1,000,000 ft of the insulated cable at the respective rates of coating (ft/min.)

		Example						Comparative Example							
		1	2	3	4	5	6	1	2	3	4	5	6	7	8
1600 (ft/min.)	spark-outs (number)	1	2	3	2	2	2	1	1	10	3	3	3	4	5
	cone-breaks (number)	0	0	0	0	0	0	0	0	3	0	0	0	0	0
	Note														
2000 (ft/min.)	spark-outs (number)	2	1	3	2	2	2	2	3	9	3	4	5	4	8
	cone-breaks (number)	0	0	0	0	0	0	0	0	4	0	0	1	0	1
	Note														
2400 (ft/min.)	spark-outs (number)	3	3	4	2	3	2	5	2	12	10	11	12	12	10
	cone-breaks (number)	0	0	0	0	0	0	1	0	5	1	1	4	2	1
	Note														
2800 (ft/min.)	spark-outs (number)	4	2	4	3	3	3	many	20	20	14	18	20	19	20
	cone-breaks (number)	0	0	0	0	0	0	21	5	7	4	4	10	10	8
	Note							imprac-tical							
3000 (ft/min.)	spark-outs (number)	2	3	3	4	3	4	-	many	many	40	38	many	many	39
	cone-breaks (number)	0	0	0	0	0	0	-	21	21	25	16	39	35	25
	Notes							-	imprac-tical	imprac-tical	imprac-tical	imprac-tical	imprac-tical	imprac-tical	imprac-tical

In Table 1, HFP/PPVE indicates the content of HFP or PPVE units expressed (% by weight) in terms of all monomer components constituting the above-described modified FEP obtained. HFP/PPVE in Table 3 is the same.

5   From Table 1 and 2, it was found that the occurrence of both spark-out and cone-breaks was reduced in each of the Examples of the present invention and these examples had superior moldability. On the contrary, the occurrence of spark-out and cone-breaks was high and the number of occurrences 10 thereof was large particularly in high-speed coating at a rate of 2800 ft/minute or higher in Comparative Examples 1 and 2 in which the MFR was less than 30 (g/10 minutes), in Comparative Example 3 in which the volatile content index was larger than 0.2 % by weight, in Comparative Example 4 in which the stress 15 relaxation modulus did not satisfy the above-mentioned formula, and in Comparative Example 5 to 8 in which the MFR was less than 30 (g/10 minutes) and/or the stress relaxation modulus did not satisfy the above-mentioned formula.

20 Example 7
   (Manufacture of a dispersion solution of an FEP copolymer containing FEP copolymer seed particles)
   A 50-L stainless autoclave with a stirrer was deaerated, and then charged with 30 kg of deaerated distilled water and 25 8 kg of a 10 % by weight of an aqueous solution of fluorine surfactant ($C_7F_{15}COONH_4$). Further, 5 kg of HFP (liquid) and then a gaseous TFE-HFP mixed monomer (TFE : HFP = 86 : 14 in weight ratio) were charged thereto. The temperature was raised gradually while stirring. As a result, the pressure of the 30 atmosphere in the autoclave was raised to 1.5 MPaG at 95 °C.
   As an initiator, 3.5 kg of an ammonium persulfate aqueous solution (APS) (10 % by weight) was charged to start the reaction. The above mixed monomer was continuously supplied to maintain the pressure at 1.5 MPaG. After 30 minutes, stirring was 35 stopped, and non-reacted TFE and HFP were collected to obtain

31.4 kg of a dispersion solution of an FEP copolymer having a solids content of 4.5 % by weight. This dispersion solution is referred to as an FEP copolymer dispersion solution containing FEP copolymer seed particles.

5   Some of the dispersion solution was coagulated using nitric acid to obtain a white powder. The composition of the copolymer thus obtained had a weight ratio of TFE : HFP = 86.0 : 14.0. It was impossible to measure the MFR, die swell and volatile content.

10 (Manufacturing of modified FEP powder)
     Next, a 50-L stainless autoclave with a stirrer was deaerated, and charged with 30 kg of deaerated distilled water. Then, 1 kg of the FEP copolymer dispersion solution containing FEP copolymer seed particles that had been prepared beforehand

15 were charged to the autoclave. Further, 6.9 kg of HFP (liquid), and then 0.2 kg of PPVE, and then a gaseous TFE-HFP mixed monomer (TFE : HFP = 86 : 14 in weight ratio) were charged thereto. The temperature was raised gradually while stirring, and the pressure of the atmosphere in the autoclave was raised to 4.2

20 MPaG at 95 °C.
     APS (10 % by weight; 1.1 kg) was then charged to start the reaction. Upon start of the reaction, a gaseous TFE-HFP mixed monomer having the same composition as mentioned above was continuously supplied to maintain a pressure of 4.2 MpaG.

25 Further, every time the amount of the TFE-HFP mixed monomer that had been supplied during reaction reached 25, 50 and 75 wt%, PPVE was charged in an amount of 20 g. Polymerization was continued until the solid content concentration of the polymer reached 20 % by weight. The total reaction time was 45 minutes.

30   Then, unreacted TFE and HFP were recovered, and the dispersion was removed and coagulated with nitric acid to obtain a white powder of modified FEP. The amount of the modified FEP dried was 7.7 kg.
     The resulting modified FEP powder as measured by the

35 methods described above was composed of TFE, HFP and PPVE units

having a weight ratio of 86.1 : 12.9 : 1.0.
(End stabilizing, pelletizing and evaluation of physical
properties)

  The modified FEP powder was heat-treated in a wet
5 condition for one hour in an end-stabilizing process and melted
for pelletizing by the method described in Example 1. A sample
was obtained by deaeration operation. The respective
measurements measured by the methods described above on the
resulting pellets showed that the MFR was 36 (g/10 minutes),
10 the volatile content index was 0.09 % by weight, and that the
stress relaxation modulus satisfied the above-mentioned
formula. The results are given in Table 3.
(Coating extrusion)

  Then, coating extrusion was performed by the method
15 described in Example 1, and spark-outs and cone-breaks were
evaluated. The results are given in Table 3.

Comparative Example 9

  In production of a modified FEP powder, the method
20 described in Example 7 was used except for supplying APS (10 %
by weight) continuously in an amount of 0.9 kg at a rate of 1.1
g/minute.

Table 3

		Example	Comparative Example
		7	9
Polymerization			
Water	(kg)	30	30
Seed (4.5%)	(kg)	1	1
Reaction temperature	(°C)	95	95
HFP	(kg)	6.9	6.9
Pressure	(MpaG)	4.2	4.2
PPVE (initial)	(kg)	0.2	0.2
PPVE (every charge)	(g)	20	20
APS (10%)	(kg)	1.1	0.9
APS (10%)(supplied continuously)	(g/min.)	0.5	1.1
Total reaction time	(min.)	45	45
Yield	(kg)	7.7	8.2
Pelletizing			
Wet heat treatment time	(min.)	60	60
Temperature of extrusion	(°C)	360	360
Extrusion rate	(kg/hour)	12	12
Deaeration time	(hours)	8	8
Characteristic of pellet			
MFR	(g/min.)	36	35
HFP/PPVE	(wt%)	12.9 / 1.0	12.9 / 1.0
Melting point	(°C)	247.3	247.5
Volatile content index	(wt%)	0.09	0.129
*1) $G(t)$ $t = 0.1$	(dyn/cm^2)	23056	17790
*2) $7 \times 10^6 \times X^{-1.62}$	(dyn/cm^2)	21081	22065
Number of spark-outs and cone-breaks per 1,000,000 ft of insulated cable at the respective coating rates (ft/min.)			
1600 (ft/min.)	spark-outs (number)	0	2
	cone-breaks (number)	0	0
2000 (ft/min.)	spark-outs (number)	0	9
	cone-breaks (number)	0	0
2400 (ft/min.)	spark-outs (number)	0	10
	cone-breaks (number)	0	0
2800 (ft/min.)	spark-outs (number)	1	18
	cone-breaks (number)	0	3
3000 (ft/min.)	spark-outs (number)	2	30
	cone-breaks (number)	0	22

*1) indicates measured values and *2) indicates a calculated value.

Table 3 shows that when the stress relaxation modulus does not satisfy the above-mentioned formula (Comparative Example 9), the occurrence of spark-outs and cone-breaks was higher as compared with Example 7, and that the occurrence thereof increased with an increase in the coating rate of the cable in Comparative Example 9 in which the amount and the rate of APS addition were changed.

INDUSTRIAL APPLICABILITY

The fluorine-containing copolymer of the present invention has a specific monomer composition as described above, an MFR of 30 (g/10 minutes) or more, a volatile content index of 0.2 % by weight or less, and a stress relaxation modulus which satisfies the above-mentioned formula. As a result, the occurrence of molding faults such as cone-breaks and spark-out are considerably reduced as compared to conventional extrusion processing over long term operation even in the case of extrusion coating electric cable with an insulating resin at high speed. In addition, the insulating material and the insulated cable thus obtained have durability to withstand long term use since they have superior physical properties such as electric characteristics and superior mechanical strength.

Accordingly, the fluorine-containing copolymer of the present invention is suitably used for extrusion coating of core materials, and in particular exerts the above-mentioned superior effects in the case of high-speed coating.

An insulating material and insulated cable formed from the above fluorine-containing copolymer are additional embodiments of the present invention.

<center>CLAIMS</center>

1.   A fluorine-containing copolymer obtained by copolymerizing tetrafluoroethylene, hexafluoropropylene and optionally perfluoro vinyl ether as component monomers,

   wherein a weight ratio of tetrafluoroethylene, hexafluoropropylene and perfluoro vinyl ether units constituting said fluorine-containing copolymer is 70 to 95 : 5 to 20 : 0 to 10, respectively;

   said fluorine-containing copolymer having:

   a melt flow rate of 30 (g/10 minutes) or more;

   a volatile content index of 0.2 % by weight or less; and

   a stress relaxation modulus $G(t)$ (unit: dyn/cm^2) which satisfies the following formula at $t = 0.1$ second when measured at a temperature of 310 °C:

$$G(0.1) > 7 \times 10^6 \times X^{-1.62} - 3000$$

where X denotes the melt flow rate (unit: g/10 minutes).

2.   The fluorine-containing copolymer as claimed in claim 1, having a stress relaxation modulus $G(t)$ (unit: dyn/cm^2) which satisfies the following formula at $t = 0.1$ second when measured at a temperature of 310 °C:

$$G(0.1) > 7 \times 10^6 \times X^{-1.62}$$

where X denotes the melt flow rate (unit: g/10 minutes).

3.   A fluorine-containing copolymer obtained by copolymerizing tetrafluoroethylene, hexafluoropropylene and optionally perfluoro vinyl ether as component monomers,

   wherein a weight ratio of tetrafluoroethylene, hexafluoropropylene and perfluoro vinyl ether units constituting said fluorine-containing copolymer is 70 to 95 : 5 to 20 : 0 to 10, respectively;

   said fluorine-containing copolymer having:

   a melt flow rate of 30 (g/10 minutes) or more;

   a volatile content index of 0.2 % by weight or less; and

<center>28</center>

a stress relaxation modulus G(t) (unit: dyn/cm^2) which satisfies the following formula at t = 0.1 second when measured at a temperature of 310 °C:

$$G(0.1) > 7 \times 10^6 \times X^{-1.6143} - 3000$$

5   where X denotes the melt flow rate (unit: g/10 minutes).

4.   The fluorine-containing copolymer as claimed in claim 3, having a stress relaxation modulus G(t) (unit: dyn/cm^2) which satisfies the following formula at t = 0.1 second when
10   measured at a temperature of 310 °C:

$$G(0.1) > 7 \times 10^6 \times X^{-1.6143}$$

where X denotes the melt flow rate (unit: g/10 minutes).

5.   The fluorine-containing copolymer as claimed in
15   claim 1, 2, 3 or 4, having a melting point of from 245 to 280 °C.

6.   The fluorine-containing copolymer as claimed in claim 1, 2, 3, 4 or 5, having a melt flow rate of from 30 to 50 (g/10 minutes).
20

7.   The fluorine-containing copolymer as claimed in claim 1, 2, 3, 4, 5 or 6, having volatile content index of 0.15 % by weight or less.

25   8.   The fluorine-containing copolymer as claimed in claim 1, 2, 3, 4, 5, 6 or 7, having a weight ratio of tetrafluoroethylene, hexafluoropropylene and perfluoro vinyl ether units of 75 to 95 : 5 to 20 : 0 to 5, respectively.

30   9.   An insulating material comprising the fluorine-containing copolymer as claimed in claim 1, 2, 3, 4, 5, 6, 7 or 8.

10.   An insulated cable comprising a core conductor
35   coated with an insulating material comprising the

fluorine-containing copolymer as claimed in claim 1, 2, 3, 4, 5, 6, 7 or 8.

11. A method of insulating cable or wire which comprises extrusion coating cable or wire with the fluorine-containing copolymer as claimed in claim 1, 2, 3, 4, 5, 6, 7 or 8.

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl⁷ C08F214/26

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
Int.Cl⁷ C08F214/26

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Japanese Utility Model Gazette 1926-1996, Japanese Publication of Unexamined Utility Model
Applications 1971-2001, Japanese Registered Utility Model Gazette 1994-2001, Japanese Gazette
Containing the Utility Model 1996-2001

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 62-192411 A (E.I.DU PONT DE NEMOURS AND COMPANY) 1987.08.24,CLAIM 1; (FAMILY:NONE)	1-11
A	JP 9-52920 A (E.I.DU PONT DE NEMOURS AND COMPANY)1997.02.25,CLAIM 1 & EP 759446 A1	1-11
A	JP 9-202814 A (E.I.DU PONT DE NEMOURS AND COMPANY)1997.08.05,CLAIMS 1-3 & US 5700889 A	1-11
A	JP 59-166516 A (DAIKIN INDUSTRIES,LTD.) 1984.09.19,CLAIMS 1-3 & EP 117450 A1	1-11
A	JP 2002-535456 A (DYNEON GMBH & CO KG) 2002.10.22,CLAIMS 1-15 & EP 1165632 A1	1-11

☑ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
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Date of the actual completion of the international search	Date of mailing of the international search report
14.04.03	30.04.03

Name and mailing address of the ISA/JP	Authorized officer	4J	9843
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Form PCT/ISA/210 (second sheet) (July 1998)

C (Continuation).	DOCUMENTS CONSIDERED TO BE RELEVANT	
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 58-69213 A (DAIKIN INDUSTRIES,LTD.) 1983.04.25,CLAIMS 1-3 & EP 75312 A2	1-11
A	WO 01/36504 A1 (DAIKIN INDUSTRIES,LTD.) 2001.05.25,CLAIMS 1-4 & EP 1262496 A1	1-11